Indian J. Phys. 75A (3), 245-247 (2001)

IJP A
— an international journal

# Electrical conductivity measurements on gel grown KDP crystals added with KCl and $KNO_3$

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*Received 8 September 2000, accepted 25 September 2000*

**Abstract** Pure and impurity added [with KCl and $KNO_3$] KDP single crystals were grown by the gel method using silica gels. Electrical conductivity measurements were carried out along both the unique axis and perpendicular directions at various temperatures ranging from 40 to 130°C by the conventional two-probe method. The present study shows that the conductivity in KDP crystals increases with the increase in impurity concentration and temperature. Activation energies were also determined and reported.

**Keywords** Electrical conductivity and impurity added KDP crystals

**PACS Nos.** 72.15.Ef, 61.72.Ss,

## 1. Introduction

Potassium dihydrogen orthophosphate, $KH_2PO_4$ (abbreviated as KDP), crystals have created considerable interest among several research workers [1-6]. A research programme on the growth and physical properties of pure and impurity added KDP crystals is on hand in this laboratory. As a part of the programme, we have studied the effect of ionic impurities [KCl, the very interesting alkali halide, and $KNO_3$, an inorganic ferroelectric material, added heavily (impurity added in the KDP solution used for the growth of crystals with impurity concentration ranging from 2000 to 10000 ppm, *i.e.* 0.2 to 1.0 mole %)] on the electrical conductivity at various temperatures ranging from 40 to 130°C of KDP crystals grown by the gel method. Already we have reported the results of our earlier study at room temperature (32°C) [7]. We report here the results obtained in our present study.

## 2. Experimental

Single crystals were grown by using the procedures reported earlier [6, 7]. Sodium metasilicate solution of density 1.08g/cc was used. Analytical reagent (AR) grade samples of the required chemicals (KDP, KCl and $KNO_3$) along with double distilled water and ethyl alcohol were used. KDP was added with KCl and $KNO_3$ separately each in six different KDP : impurity molecular ratios, *viz.* 1:0.000 (pure KDP), 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010.

Scalenohedral morphology (twelve sided polyhedron) was exhibited by all the crystals grown. All the grown crystals were found to be very stable, colourless and transparent. Crystals with high transparency and large defect-free size (> 3 mm) were selected and used for the electrical conductivity measurements. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good ohmic contact.

The conductivity measurements were carried out along both the unique axis (c-) and perpendicular (a- and b-) directions for all the eleven crystals grown using the conventional two-probe technique at various temperatures ranging from 40 to 130°C. The resistance of the crystals were measured using a Meco multimeter. The observations were made while cooling the sample. The dimensions of the crystals were measured using a travelling microscope (L. C. = 0.001 cm). The conductivity ($\sigma$) of the crystal was calculated using the relation

$$\sigma = \frac{\ell}{RA}$$

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where $R$ is the measured resistance, $d$ the thickness of the sample and $A$ the area of the face in contact with the electrode.

Plots between $\ln(\sigma T)$ and 1000/T were found to be very nearly linear. So, the conductivity values can be fitted to the relation

$$\sigma T = \sigma_0 \exp(-E/kT),$$

where $E$ is the activation energy, $k$ the Boltzmann constant, $T$ the absolute temperature and $\sigma_0$ the parameter depending on the material. Activation energies were estimated using the slopes of the above line plots [$E$ = – (slope) k × 1000 ].

When the crystals are grown in gel media, there is a possibility that the conductivity and related properties are different for different crystals even though they are grown in the same container. It would be better if there is a possibility to estimate quantitatively the concentration level of the impurity that is present in each crystal. But, it is very difficult to do so since the impurity concentration is < 1%. Hence, in order to understand qualitatively (atleast) whether the added impurity has entered into the KDP lattice or not, we carried out the density measurement by using the floatation technique.

## 3. Results and discussion

It was observed that the difference in densities of crystals grown in the same container was very small and negligible. Average densities are given in Table 1. The value observed for pure KDP (2.344 g/cc) compares well with that reported in the literature (2.338 g/cc) [8]. The observed decrease of density of KDP crystal caused by the impurities indicates that the impurities have entered into the lattice of KDP crystals. Moreover, it can be seen that the density decreases further with the increase in impurity concentration of the aqueous solution of KDP used for the growth of crystals.

**Table 1.** Densities and activation energies

| System (impurity in mole%) | Density (g/cc) | Activation energy, E(eV) along a-direction | c-direction |
|---|---|---|---|
| (a) Pure KDP | 2 344 | 0.220 | 0.216 |
| (b) KCl added KDP | | | |
| 0.2 | 2.233 | 0 427 | 0 389 |
| 0.4 | 2.223 | 0.438 | 0 393 |
| 0.6 | 2.220 | 0.430 | 0 413 |
| 0.8 | 2.193 | 0.415 | 0 406 |
| 1.0 | 2.192 | 0.381 | 0.370 |
| (c) $KNO_3$ added KDP | | | |
| 0.2 | 2.297 | 0.391 | 0.390 |
| 0.4 | 2.288 | 0.384 | 0.344 |
| 0.6 | 2.278 | 0.389 | 0 347 |
| 0.8 | 2.259 | 0.399 | 0.336 |
| 1.0 | 2.242 | 0.405 | 0.338 |

The $\sigma$ values obtained along the two directions (a- and b-) perpendicular to the unique axis (c-direction) are, within experimental error, the same. Figures 1-4 show the plots of $\ln(\sigma T)$ against 1000/T for the pure and impurity added KDP crystals. The values of the activation energy E for pure and impurity added KDP crystals are given in Table 1.

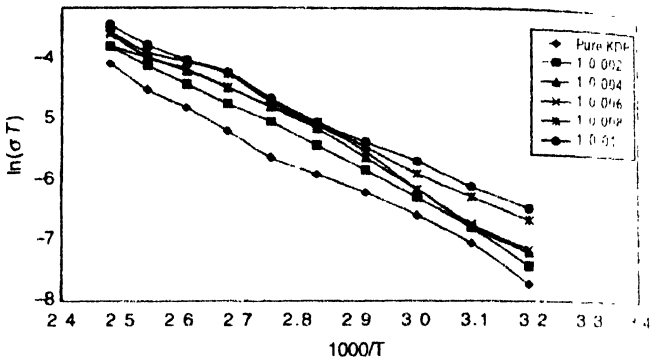


**Figure 1.** Variation of $\ln(\sigma T)$ with 1000/T along a-direction for KCl added KDP

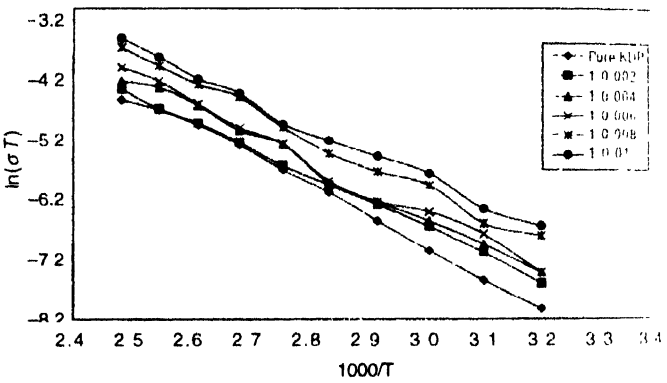


**Figure 2.** Variation of $\ln(\sigma T)$ with 1000/T along c-direction for KCl added KDP.

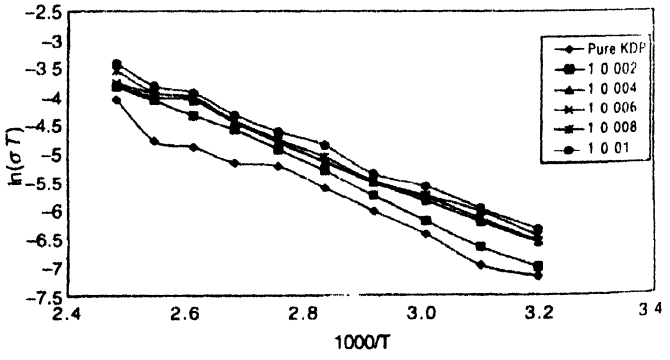


**Figure 3.** Variation of $\ln(\sigma T)$ with 1000/T along a-direction for KNO added KDP.

Conductivities obtained in the present study, are of the same order with those obtained by previous authors for the KDP crystals (× $10^6$ mho/metre) [2,5-7, 9,10].

It can be seen that for both the impurities considered in the present study, the electrical conductivity increases with the increase in impurity concentration and temperature. This is

similar to that observed for oxalate [2] and ammonium compound [6] added KDP crystals. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The addition of impurity further increases the electrical conduction in the temperature region considered. This can be explained by considering the replacement of $(H_2PO_4)^{-1}$ ions by $Cl^{-1}$ and $(NO_3)^{-1}$ ions.

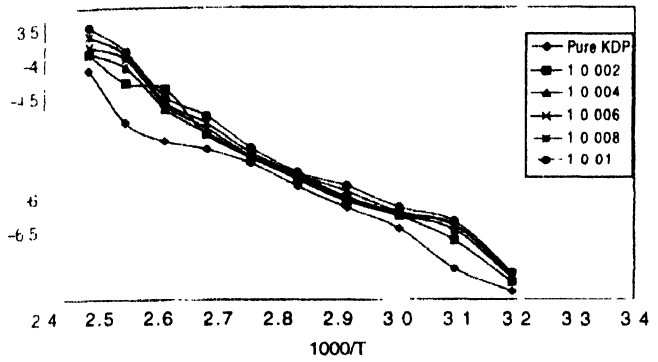


Figure 4. Variation on $\ln(\sigma T)$ with 1000/T along c-direction for $KNO_3$ added KDP

The electrical conduction in KDP crystals has been established [11-12] to be protonic. In KDP type of crystals, the possible type of point defects which help the electrical conduction process are the ionization defects, *viz* $(HPO_4)^{2}$ and $H_2PO_4$, produced as a result of proton jump from one phosphate group to another along the same bond [13] and L and D defects.

Jaccard and his coworkers [14, 15] have shown that proton conduction may be accounted for by motion of protons accompanied by a *D* defect (excess of positive charge). Migration of these defects may only modify electric polarization and may not change the charge at an electrode [14]. The motion of defects occurs by some kind of rotation in the bond with defects. The speed of displacement $v = \upsilon a$, where $a$ and $\upsilon$ are the distance and frequency respectively of the jump from one bond to the other.

If the sample crystal is placed in a stationary electric field (as in the present study), the carriers may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure, they accumulate in the regions close to the plates which causes a concentration gradient to be formed and this gradient feeds a diffusion current. At equilibrium, the diffusion current density equals that of the drift current. Charge accumulation is related to inhomogeneities of the material, the agglomeration of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes [16].

The conductivities are more along the *a*-direction than those along the *c*-direction for both the impurities considered in the present study for all the impurity concentrations and all temperatures considered. This is in correspondence with the results obtained by the previous authors for their systems [2,6,9].

The E values are more along *a*-direction than those along *c*-direction for both the impurities for all the impurity concentrations. However, there is no systematic variation observed with the impurity concentration.

The conduction region considered in the present study, seems to be connected to mobility of vacancies. The low activation energies observed suggests that oxygen vacancies may be responsible for conduction in this region. The present study gives further evidence to the statements : i) the electrical conduction in KDP crystals is protonic ; and ii) the electrical conduction in KDP crystals is mainly due to the anions *viz* $(H_2PO_4)^{-1}$ ions and not the cations *viz*. $K^+$ ions.

## 4. Conclusions

Pure and impurity (KCl and $KNO_3$) added KDP single crystals were grown and electrical conductivities were measured along both the *a*- and *c*- directions at various temperatures ranging from 40 to 130°C. Density measurement indicates that the impurity molecules have entered into the lattice of KDP crystals. The present study gives further evidence to prove that the conduction in KDP is protonic and mainly due to the anions and not the cations. The present study indicates that the conductivity increases with the increase in impurity concentration and temperature. At low temperatures, the conductivities are more along the *a*-direction than those along the *c*-direction.

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